(12) EUROPEAN PATENT APPLICATION

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(54) **Manufactured articles in silicon oxide and/or other mixed metallic oxides and process for their preparation in "final" or "almost final" dimensions**

(57) Optical components are described, in silicon oxide and/or other mixed metallic oxides having dimensional precision which has a tolerance of surface roughness and profilometric accuracy within the specifications described for visible and ultraviolet spectrum ranges. The above manufactured articles have "final" or "almost final" dimensions as they are obtained by the isotropic dimensional reduction (miniaturization) of amorphous monolithic materials, called aerogels, which are in turn prepared by cold moulding techniques based on sol-gel processes.

These objects are particularly used as accessories for thermal treatment in the electronic or ceramic industries and/or as optical components and devices.

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EP 0 705 797 A2

Description

The present invention relates to optical components in silicon oxide and/or other mixed metallic oxides having dimensional precision which has surface roughness tolerance and profilometric accuracy within the specifications described for visible and ultraviolet spectrum ranges.

The above manufactured articles have "final" or "almost final" dimensions as they are obtained by the isotropic dimensional reduction (miniaturization) of amorphous monolithic materials, called aerogels, in turn prepared by means of cold moulding techniques based on sol-gel processes.

The process for the preparation of the above objects involves the accurate geometrical definition of the aerogel by:

- the cold filling of a suitable mould with a liquid colloidal dispersion, called sol, formed from specific chemical precursors;
- the polycondensation of the sol to obtain the respective gels therefrom (gelation);
- the supercritical drying of the gels until aerogels are obtained with dimensions corresponding to the mould used;
- the isotropic reduction (miniaturization) of the amorphous monolithic aerogels thus obtained, consisting of silicon oxide alone or in the presence of one or more oxides of elements belonging to groups III° to VI° of the Periodical Table and exceptionally also other groups.

It is known that optical materials, and in particular transparent optical materials such as silica or molten quartz and optical glass, owing to their hardness and fragility, are difficult to process as the direct hot moulding of these optical components and devices is generally not possible for reasons of product quality.

The traditional method for producing these optical elements is based on the reduction of an adequate preform to the end product by means of slow, precise grinding operations.

Whereas some of these operations, such as reduction with both a flat and spherical surface, can be automized, others, such as aspherical finishing, require complicated manual processes.

This operational difficulty results in a limited process flexibility on an industrial scale and unreasonably high costs to obtain quality products such as optical components and devices based on the above aspherical optical system.

Owing to these technological limitations the optical industry has tried to solve the problem in various ways.

One of these is the moulding at high pressure and temperature of aspherical lenses and other optical components, directly from appropriate preforms of the optical material desired; with this method, which requires extremely sophisticated equipment such as a hot hydrostatic press, high quality products are obtained but also at a high cost and the process consequently necessitates very substantial investments.

One way of reducing the costs is by the use of organic optical materials, in particular plastics.

These materials can be melted and moulded with much more economical processes and can also be very easily processed with machine tools.

Unfortunately the dimensional precision of the optical products obtained generally by melting, is negatively influenced both by the insufficiently controllable shrinking of the material during the cooling operation and by the change of liquid-solid phase which causes a dimensional distorsion and deterioration of the optical quality of the manufactured article.

Also with the use of mechanical processing with machine tools, the optical products obtained from plastic materials do not have an acceptable quality as the material cannot be accurately processes owing to the fact that it is too soft.

In addition, the products which can be obtained with the above plastic materials, by hot moulding or mechanical processing, suffer from limited chemical and dimensional stability and do not reach the durability standards established for inorganic optical materials.

It is also known that optical components with definite dimensions can be obtained by suitably treating a gel deriving from the hydrolysis of a silicon alkoxide.

For example, U.S. patent 4.680.049 describes a method for the preparation of optical glass based on silicon oxide which involves an initial hydrolysis of a silicon alkoxide, the drying of the above gel and a final thermal syntherization treatment until an optical glass with definite dimensions is obtained.

These "final" optical products however have a very significant deviation with respect to the profile of the aerogel, as is amply illustrated in Figure 1.

The two diagrams shown in the above figure represent the configuration of the upper surface of the aerogel (diagram A) and the corresponding surface of the densified product (diagram B) respectively.

In the mould in which the gel is prepared the corresponding surface is rigorously flat: it can be seen how the flat surface of the mould passes to a convex surface in the aerogel to end up as a concave surface in the densified product.

The distorsion of the manufactured article is herein quantified as follows:

$$\text{- distortion from mould to aerogel} = \frac{20\mu m}{3000\,\mu m} \times 100 = 0.67\%$$

$$\text{- distortion from aerogel to glass} = \frac{40\mu m}{2000\ \mu m} \times 100 = 2\%$$

This process, which herein is simply indicated as "compensated distorsion process", is severely limited in its
industrial applications as there are difficulties in programming specific geometries of the product.

In fact, as there is no biunivocal, continuous correspondence between the geometry of the mould and that of the
product, there is also no rational control of the final dimensions of the product itself.

Another attempt at developing the processing technology of optical materials has been made using machine tools
with a very high precision numerical control, having a diamond point so as to be also able to process hard materials
such as quartz and optical glass and with movement on air bearings to minimize the vibrations of the tool point.

These machines have been successfully developed in the last ten years and reach precision in the profile control
of about a tenth of a micrometer and, under favourable conditions, even higher precision in the control of the surface
roughness; they are consequently capable of finishing an item with so-called "optical" precision, which means a precision
which is suitable for optics limited within the infrared spectrum range.

On the other hand, the above machines are still not adequate for applications in visible and ultraviolet spectrum
ranges owing to the more severe specifications of surface roughness and profilometric accuracy required by optical laws
within these spectrum ranges.

In addition, this high precision processing, which although economically convenient in special applications such as
mirror finishing by laser in copper, aluminium or other materials typically used in infrared, is not generally economical
for obtaining transparent optical components based on silica or inorganic glass, for numerous reasons including the
hardness and fragility of the materials.

It is known in fact that these machines can be well used in the processing of typical materials for applications in
infrared; this is due to their processability characteristics which are much higher than optical glass.

This creates great difficulties in the spectrum ranges, where glass is the prevalent material for which the technology
of the single rotating diamond point (S.P.T.D.M.) cannot be used because of its fragility.

As described in Italian patent application MI-92A02038 filed by the Applicant, these high precision machine tools
are used on intermediates to obtain perfectly and completely isotropic optical components and devices in "final" or
"almost final" dimensions; the above intermediates, as they have the property of isotropically shrinking, are monolithic
aerogels ideally amorphous of silica and/or other metallic oxides produced according to the technolgy described in U.S.
patent 5.297.814.

The Applicant has now found that gels prepared with the technology of U.S. patent 5.207.814, in suitable moulds,
in accordance with what is described in Italian patent application MI92A02038 which can be referred to for any possible
point of interest, can be linearly miniaturized into densified products which maintain the proportions of the mould with a
precision greater than one part out of 10,000.

In particular, therefore, the invention relates to the preparation of the above products, according to a process which
involves the accurate geometrical definition of the aerogel by:

- the cold filling of a suitable mould with a liquid colloidal dispersion, called sol, formed from specific chemical pre-
cursors;
- the polycondensation of the sol to obtain gels (gelation);
- the supercritical drying of the gels until aerogels are obtained with dimensions corresponding to the mould used;
- the isotropic reduction (miniaturization) of the amorphous monolithic aerogels thus obtained, consisting of silicon
oxide alone or in the presence of one or more oxides of elements belonging to the III° to VI° Group of the Periodical
Table and exceptionally also other groups.

These cold moulding techniques are based on the use of special specifically prepared moulds.

These moulds, having much greater dimensions than the manufactured article, have an internal volume which is
defined as a "homothetic copy" of the "end"-product itself, which is characterized in terms of profilometric accuracy,
surface roughness and scaling ratio with the product itself.

The product thus obtained has "almost final" dimensions i.e. it requires only an optical polishing with the conventional
methods or, at the best, it has "final" dimensions i.e. it does not require any conventional optical processing.

The overall result of the present invention is therefore the economical production of optical components and devices
made of silica glass or other optical glass using a new cold moulding technique based on specific sol-gel synthesis
processes.

The present invention consequently relates to optical articles, components or devices, with "final" or "almost final"
dimensions and completely isotropic, consisting of silicon oxide, either alone or in the presence of one or more oxides
belonging to groups III° to VI° of the Periodic Table, and exceptionally also other groups, said optical articles, components
or devices having dimensional precision which has tolerance to surface roughness and profilometric accuracy required
for the visible and ultraviolet spectrum ranges, characterized in that said tolerance being between 1/2 and 1/10 wave

length corresponding to the range 0.350-0.02 micrometers and, preferably, equal to 1/4 wave length corresponding on an average, in the visible range, to 0.275 micrometers.

The above and other operating details will be explained in the following illustrative examples which however do not restrict the scope of the present invention.

EXAMPLE 1

PREPARATION OF PREFORMS OF PURE SILICA

An example is given of the preparation of silica glass disks, with a diameter of 2.5 cm and height of 1.0 cm, as preforms for optical lenses.

For this purpose, 80 ml of HCl 0.01N are added, under vigorous stirring, to 100 ml (0.44 moles) of tetraethylorthosilicate (TEOS) (molar ratio TEOS:H_2O:HCl=1:10:1.8 x10^{-4}).

After about 60 minutes a limpid solution is obtained and 52.8 g of colloidal silica powder (Aerosil OX50 - Degussa) prepared from silicon tetrachloride by oxidation at high temperatures, is added, still under vigorous stirring, to this solution.

The mixture obtained is homogenized using ultra-sounds for a duration of about ten minutes and then clarified by centrifugation.

The homogeneous dispersion obtained is poured into cylindrical containers of polyester with a diameter of 5.0 cm and height of 2.0 cm, which are hermetically closed, placed in an oven and maintained at 50°C for 12 hours.

The gel which is obtained is suitably washed with ethanol and subsequently supercritically dried in an autoclave at a temperature of 300°C or in any case higher than the critical temperature of the solvent.

An aerogel is obtained which is calcinated at a temperature of 800°C in an oxidizing atmosphere.

During the heating, the residual organic products coming from the treatment in the autoclave are burnt.

The dimensions of the aerogel obtained are those of the internal volume of the initial cylindrical container.

The disk of silica aerogel, after calcination, is subjected to a stream of helium containing 2% of chlorine, at a temperature of 800°C and for a duration of 30 minutes to remove the silanolic groups present; the aerogel disk is finally heated in a helium atmosphere to a temperature of 1400°C for the duration of one hour so that the silica reaches complete densification and consequent miniaturization.

After cooling, the disk reaches the desired final dimensions (diameter 2.5 cm and height 1.0 cm), maintaining a homothetic ratio with the form of the initial aerogel determined by the initial mould.

The densified material has the same physicochemical characteristics as the silica glass obtained by melting (density=2.20; refraction index (at 587.56 nm)= 1.4585; Abbe dispersion=67.6).

EXAMPLE 2

DUPLICATION OF OPTICAL SURFACES.

Moulds are prepared with an internal surface finished with optical specifications (surface roughness less than 1/5 with a wave length corresponding to less than 0.08 micrometers).

The internal volume of the moulds corresponds to a cylinder of 5.0 cm in diameter and 2.0 cm in height.

One of the bases of the cylinder consists of the optical surface to be duplicated.

A colloidal solution prepared by adding to the homogeneous solution, obtained as in example 1, a solution of ammonium hydroxide 0.1N, dropwise under stirring, until a pH of about 4-5 is reached, is poured into the moulds.

The moulds thus filled, are hermetically closed, placed in an oven and maintained at 20°C for 12 hours.

The production of the gel and subsequent supercritical drying are carried out according to the procedure described in example 1.

The profilometric and surface roughness results, measured on the optical surface of the aerogel, have the same optical quality as the original surface with a roughness of less than 0.1 micrometres, corresponding to 1/5 average wave length of the visible spectrum range.

EXAMPLE 3

ASPHERICAL LENSES

A mould has been designed for providing a preform for a flat/convex lens of which the convex surface corresponds to an aspherical surface defined by the general equation:

$$X = \frac{cy^2}{1 +\sqrt{1-(K+1)c^2y^2}}+Dy^4 + Ey^6 + Fy^8 + Gy^{10}$$

wherein the y axis of the equation corresponds to the optical axis of the lens.

The constants for the densified product, having a diameter of 15 mm± 0.05 and height of 6.25 mm± 0.10, are the following:

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- C= 0.17364596
- K= -1.000000
- D= -0.000071
- E= 0.000022
- F= -6.62323E^{-7}
10
- G= 7.03174E^{-9}

To obtain the specific dimensions of the densified product, a miniaturization factor was programmed equal to 2, which is equivalent to an internal mould volume with double dimensions with respect to the manufactured article desired.

The transformations for the new constants are:

15
- C'= C/R
- K'= K
- D'= D/R^3
- E'= E/R^5
20
- F'= F/R^7
- G'= G/R^8

The appropriate mould was prepared with machine tools having numerical control.

No optical finishing treatment was carried out on the surface of the mould, the objective of the experiment being the
25 average profile of the aspherical lens rather than the optical finishing of the surface.

A silicic sol was prepared with the procedure of example 2.

A series of 3 aerogels was prepared using the above mould according to the procedures described in example 2.

The aerogels were subjected to profilometric analysis as follows: each aerogel was placed in line at the centre of a Mitutoyo series 332 profile projector and compared to the theoretical profile corresponding to the equation of the aspher-
30 ical profile.

The comparison was carried out by direct placement over the screen.

To increase the sensitivity of the method, each analysis was carried out with photographic aid and subsequent projection on a huge screen providing a sensitivity of up to a ten thousandth of the dimension of the object.

The aerogels were then densified (miniaturized), with the thermal treatment described in example 1 and compared
35 with the respective theoretical profile as in the case of the aerogels.

In both the aerogels and the densified products, the maximum deviation, relating to the respective theoretical profiles is less than 0.002 mm, a value which is considered as the limit of the sensitivity of the method.

An example of profilometric determination is shown in Figure 2 wherein the aspherical profile of the aerogel is comparable to the theoretical profile generated by the equation (see the dark external line) and the site of the theoretical
40 profile points has been slightly moved towards the outside to facilitate observation of the trend parallel to the surface.

In addition to the profilometric analysis, the dimensional reproducibility was verified, by micrometry, on the main diameters (flat surface) of the densified products.

The results are summarized in Table 1 below:

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TABLE 1

SAMPLE	AVERAGE DIAMETER(mm)	STAND. DEVIATION
A 34/44-1	15.3775	0.003
A 34/26	15.3725	0.002
A 34/28	15.3780	0.003

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55 Claims

1. Optical article, in "final" or "almost final" dimensions and completely isotropic, consisting of silicon oxide, either alone or in the presence of one or more oxides of elements belonging to groups III° to VI° of the Periodic Table, said article having dimensional precision which has tolerance to surface roughness and profilometric accuracy required for

visible and ultraviolet spectrum ranges, characterized in that said tolerance is between 1/2 and 1/10 wave length corresponding to the range 0.350-0.02 micrometres.

2. Optical article, according to claim 1, which has a tolerance equal to 1/4 wave length corresponding, in the visible range, to 0.275 micrometres.

3. Optical article, according to claim 1, consisting of silicon oxide and a second oxide, the latter being selected from germanium oxide and titanium oxide.

4. Use of articles, according to claims 1 to 3, in optical systems.

5. Manufactured article with a high precision of "final" or "almost final" dimensions and completely isotropic, consisting of silicon oxide, either alone or in the presence of one or more elements belonging to groups III° to VI° of the Periodic Table, said article having dimensional precision which has a tolerance to surface roughness and profilometric accuracy required for visible and ultraviolet spectrum ranges, characterized in that this tolerance is between 1/2 and 1/10 wave length corresponding to the range 0.350-0.02 micrometres.

6. High precision manufactured article, according to claim 5, which has a tolerance equal to 1/4 wave length corresponding, in the visible range, to 0.275 micrometres.

7. High precision manufactured article, according to claim 5, consisting of silicon oxide and a second oxide, the latter being selected from germanium oxide and titanium oxide.

8. Use of the manufactured articles, according to claims 5 to 7, as accessories in the electronic or ceramic industries.

FIG. 1

MEAN DEVIATION
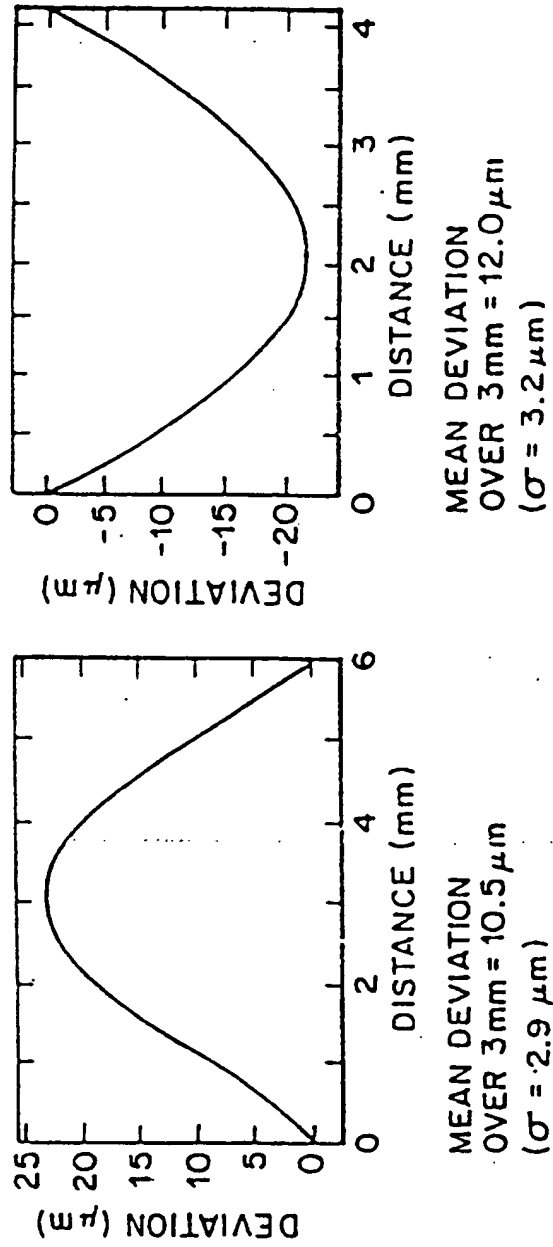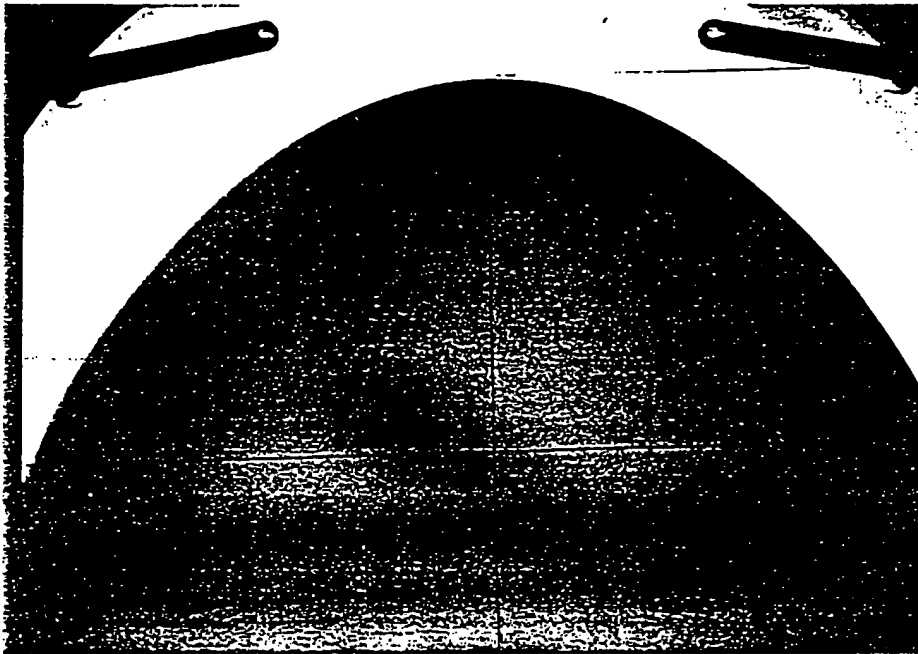OVER 3mm = 12.0 μm
(σ = 3.2 μm)

MEAN DEVIATION
OVER 3mm = 10.5 μm
(σ = 2.9 μm)

FIG. 2